pubs.acs.org/JACS

Atomically Dispersed Ni/ α -MoC Catalyst for Hydrogen Production from Methanol/Water

Lili Lin,[•] Qiaolin Yu,[•] Mi Peng,[•] Aowen Li,[•] Siyu Yao, Shuheng Tian, Xi Liu, Ang Li, Zheng Jiang, Rui Gao,^{*} Xiaodong Han, Yong-wang Li, Xiao-dong Wen, Wu Zhou,^{*} and Ding Ma^{*}



ABSTRACT: Methanol–water reforming is a promising solution for H_2 production/transportation in stationary and mobile hydrogen applications. Developing inexpensive catalysts with sufficiently high activity, selectivity, and stability remains challenging. In this paper, nickel-supported over face-centered cubic (fcc) phase α -MoC has been discovered to exhibit extraordinary hydrogen production activity in the aqueous-phase methanol reforming reaction. Under optimized condition, the hydrogen production rate of 2% Ni/ α -MoC is about 6 times higher than that of conventional noble metal 2% Pt/Al₂O₃ catalyst. We demonstrate that Ni is atomically dispersed over α -MoC via carbon bridge bonds, forming a Ni₁–C_x motif on the carbide surface. Such Ni₁–C_x motifs can effectively stabilize the isolated Ni₁ sites over the α -MoC substrate, rendering maximized active site

or $CH_3OH(I)+H_2O(I)\rightarrow 3H_2(g)+CO_2(g)$



density and high structural stability. In addition, the synergy between Ni_1-C_x motif and α -MoC produces an active interfacial structure for water dissociation, methanol activation, and successive reforming processes with compatible activity.

INTRODUCTION

Hydrogen transportation, distribution, and storage at different scales in an efficient and reliable way remains technically and economically challenging,1-3 which hinders the extensive utilization of polymer electrolyte membrane fuel cells (PEMFCs) in stationary and mobile applications.^{4,5} It has been proposed that hydrogen stored in a chemical form and released in situ on demand through efficient catalytic processes provides a promising solution for hydrogen storage and application.⁶⁻⁸ Compared with other liquid organic (such as quinoline and carbazole, etc.) and inorganic (such as NH₃ and borane, etc.) hydrogen carriers, methanol, an important inexpensive bulk chemical, is able to react with water and release 3-fold H₂ (CH₃OH + H₂O=CO₂ + 3H₂) under relatively mild condition, achieving a high H₂ gravimetric density of 18.8% by weight. The well-balanced high H₂ storage capacity and mild H₂ release condition make methanol one of the most attractive liquid forms of H₂ carrier candidates.^{9,10} Methanol reforming in the aqueous phase can remove the tedious vaporization units from the hydrogen production device, thus improving economic efficiency. It can also take advantage of intensified water gas shift reaction (WGSR) to effectively suppress the selectivity toward byproduct CO.¹¹⁻¹³

The pioneer works have demonstrated that hydrogen can be generated through aqueous-phase methanol reforming over platinum- and ruthenium-based noble metal catalysts.^{9,13,14} Recently, we proposed that a new noble metal catalyst, Pt/α -

MoC, is highly active for this reaction at low temperatures. The efficient C–H and O–H activation ability and the highly effective interfacial water gas shift activity of Pt/ α -MoC render to the catalyst an excellent hydrogen evolution rate of 18 000 h^{-1.10} Despite the excellent activity, the high cost and limited reserve of noble metals are still the big obstacles for large-scale applications. Therefore, developing efficient non-noble-metal catalytic systems capable of working in an aqueous phase with high reactivity is highly desirable but challenging.

Herein, a novel Ni/ α -MoC catalyst is reported to effectively catalyze the methanol reforming reaction with high activity and selectivity in aqueous solution below 240 °C. Nickel is atomically dispersed over an α -MoC surface, creating isolated Ni sites anchored over α -MoC host via carbon bridge bonds, forming Ni₁-C_x motifs with ultrahigh site density (up to 2 wt % loading of Ni). The 2% Ni/ α -MoC catalyst shows a high hydrogen evolution activity of 171 μ mol_{H2}/g_{cat}/s (ATOF = 1805 h⁻¹) at 240 °C, which is around 6 times higher than that of the conventional 2% Pt/Al₂O₃ and the most active nonnoble-metal catalyst reported so far.¹³ The high activity is

Received: October 12, 2020 Published: December 28, 2020



Article





Figure 1. Structure characterization of the as-prepared Ni/ α -MoC catalysts. (a) XRD profiles of the Ni/ α -MoC with different Ni loadings. (b) *In* situ XPS of 0.5%, 2%, and 7% Ni/ α -MoC catalysts. The Ni 2p, C 1s, and Mo 3d regions are presented. (c) Ni K edge XANES spectra of 0.5%, 2%, 3%, 5%, and 7% Ni/ α -MoC catalysts along with Ni foil and Ni oxide. The enlarged XANES white-line and pre-edge region are shown in the right panel. (d) Ni K edge EXAFS spectra and fittings of 0.5%, 2%, 3%, 5%, and 7% Ni/ α -MoC catalysts.

attributed to the synergy effect of the Ni₁– C_x motif and α -MoC host with highly effective water dissociation capability.

RESULTS AND DISCUSSION

 α -MoC was prepared from MoO₃ through successive NH₃ ammonization and CH₄/H₂ reduction treatments.^{10,15} Ni precursors were deposited over the as-synthesized molybdenum carbide support using a wetness impregnation method under the protection of Ar. After the carburization activation at 590 °C in the flow of a CH₄-H₂ mixture, the as-prepared Ni/ α -MoC catalysts were obtained. The exact Ni loadings were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Table S1). The X-ray diffraction (XRD) profiles of the Ni/ α -MoC catalysts show only the diffractions of α -MoC (Figure 1a). Even when the loading of Ni was increased to 7 wt %, no diffraction peaks associated with bulk Ni crystal were observed, indicating that the Ni species are highly dispersed over the substrate with the crystalline domains below the detection limit of XRD.^{16,17}

The Ni 2p X-ray photoelectron spectroscopy (XPS) results reveal that overall the Ni species in those samples are closer to metallic Ni. However, a positive shift of the Ni 2p binding energy was observed over 2% Ni/ α -MoC, which is 0.6 eV higher than that of metallic Ni(0)¹⁸ as shown in Figure 1b (853.3 vs 852.7 eV). Although the final state effects may affect the binding energy shift in XPS, the α -MoC support used here is a conductive material, and therefore, the final state effect (screening) is less important compared to the nonconductive substrate. Therefore, it is highly possible that the blue shift is possibly an indication of charge transfer from Ni to α -MoC and suggests that the electronic structure of the Ni species is modulated by α -MoC.¹⁹ With increasing Ni loading, the shift of the Ni binding energy reduces to 0.3 eV at 7% Ni/ α -MoC (Figure 1b, inset), due to less average charge being transferred to the substrate and the emergence of more metallic character of the Ni species. This is in good agreement with our theoretical calculations that isolated Ni atoms transfer more charges to the α -MoC substrate per Ni atom than those in Ni particles (Figure S1).

The charge transfer and interaction between Ni and α -MoC was further confirmed by the X-ray absorption fine structure spectroscopy (XAFS) experiments. The Ni K edge (8333 eV) X-ray absorption near-edge structure (XANES) spectra of all the Ni/ α -MoC catalysts show stronger white-line intensity and slightly blue-shifted edge position as compared to Ni foil (Figure 1c; notice that they are different from that of NiO), demonstrating that the supported Ni is close to the metallic Ni) but under an electron-deficient state (namely, Ni^{δ +}).^{20,21} A lower white-line intensity was observed over the 7% Ni/ α -MoC catalyst, as compared to that of 0.5% Ni/ α -MoC, suggesting the recurrence of the metal character.²²

We further investigated the local chemical environment of the Ni species by analysis of the extended X-ray absorption fine structure (EXAFS). Significantly, no Ni–Ni first-shell scattering was resolved in the EXAFS profiles of the 0.5% and 2% Ni/ α -MoC catalysts (Figure 1d), indicating that nearly 100% of the Ni species are isolated Ni atoms over α -MoC in these two catalysts. For the 0.5% and 2% Ni/ α -MoC catalysts, the major



Figure 2. Electron microscopy characterization of the 2% Ni/ α -MoC catalyst. (a) Low-magnification STEM-HAADF image. High-magnification (b) STEM-HAADF and (c) STEM-BF images. (d) STEM-HAADF image and the corresponding EDS elemental maps of (e) Ni and (f) Mo of 2% Ni/ α -MoC. Ni is homogeneously distributed within the sample. (g) STEM-HAADF image and (h) the corresponding EELS Ni map. Ni single atoms are indicated by the green circles. An occasional Ni cluster is indicated by the blue circle. (i) Overlay of the distribution of Ni on α -MoC. (j) The enlarged Ni elemental map and the corresponding pixel index of the area marked by the green dashed square in panel h. The lateral size of each pixel is 0.15 nm. (k) The EELS spectra extracted from the pixels with the corresponding colors in panel *j*, demonstrating that Ni signals are localized in the central pixel as expected for an atomically dispersed Ni atom. (l) Comparison of the sum spectrum from 33 Ni single atoms and the reference spectra of metallic Ni and NiO.

pubs.acs.org/JACS

Article

Table	1.	Catalytic	Performance	of Aqueous	Methanol	Reforming	over	Nickel-Based	Catalysts"
-------	----	-----------	-------------	------------	----------	-----------	------	--------------	------------

entry	catalysts	temp (°C)	mass-specific activity $\mu mol_{H2}/g/s^b$	ATOF ^c	selectivity (CO) %
1	2% Ni/α-MoC	240	171	1805	0.7
2^d	2% Pt/Al ₂ O ₃	240	30.7	1077	0.4
3	2% Ni/MoO ₃	240	4.94	33	11.5
4	2% Ni/MoO ₂	240	8.35	54	15.7
5	2% Ni/TiO ₂	240	5.8	43	16.6
6	2% Ni/SiO ₂	240	7.8	49	26.8
7	Ni(acac) ₂	240		9.2	11.6
8 ^e	NiAl–Au (SRM) ^f	280	54.3		28.9
9 ^e	NiAl-Au (SRM) ^f	340	128.7		29.0
10 ^e	Cu/ZnO/Al ₂ O ₃ (SRM) ^g	250	109		1.0

^{*a*}Reaction conditions: $n(CH_3OH)/n(H_2O) = 1:1, 50$ mL of total volume of liquid, 100 mg of activated catalysts; 2 MPa of N₂ (10% Ar as internal standard). All the conversions are controlled below 15%. Detailed experimental parameters are shown in the Supporting Information. ^{*b*}Catalytic performance is calculated as the hydrogen production per gram of catalyst per second. The unit is μ mol_{H2}/g_{cat}/s. ^{*c*}ATOF means average turnover frequency number; the unit is mol_{H2}/mol_{metal}/h. The molar amount of metal is the amount of loaded metal determined by ICP-AES. ^{*d*}The hydrogen production activity of 2% Pt/Al₂O₃ is in good agreement with the reported value in literature (ref 13). ^{*e*}The reaction data was collected from refs 27 and 30. SRM: steam reforming of methanol. ^{*f*}Ref 27. ^{*g*}Refs 28 and 30.

neighbors of Ni are C and Mo (Table S2, Figure S2). The Ni-C bond length is around 2.01 Å, while the Ni-Mo coordination shells below 2.70 Å and above 2.85 Å are attributed to the Mo atoms located at the subsurface of C atoms (see models I and II in Figure S3). The presence of Ni-C coordination over the 0.5% and 2% Ni/ α -MoC catalysts indicates that the isolated Ni atoms are anchored over the α -MoC surface with carbon as bridges (termed as the Ni_1-C_x motif) (see possible configurations in Figure S3). As Ni tends to form nickel carbide in a carbon-rich environment,^{23,24} the strong bonding between Ni and carbon can be expected. The density functional theory (DFT) calculations also confirm that the Ni atoms connecting with α -MoC through carbon bridges are energetically favorable (see Table S3). When the loading of Ni is sufficiently low (in this case, no more than 2%), the strong nickel-carbon bonding confers to the Ni/α-MoC catalyst a unique conformation, with the isolated Ni species anchoring over α -MoC via the Ni₁-C_r motifs. This unique arrangement of Ni1 species over molybdenum carbide has not been reported before and is different from that of Pt/α -MoC,^{10,19} in which Pt is atomically dispersed over the α -MoC substrate with only the Pt-Mo coordination. When the Ni loading is increased to 3% and 5%, the Ni-Ni scattering emerges with coordination numbers (CN_{Ni-Ni}) of 0.9 and 3.4, respectively, suggesting the formation of Ni clusters or even small nanoparticles. As these Ni-Ni coordination numbers are still small, it is reasonable to attribute them to the occasionally observed small Ni particles in the scanning transmission electron microscopy (STEM) images (see discussions below), while the majority of the Ni species in the 3% and 5%Ni/ α -MoC are still atomically dispersed $Ni_1 - C_x$ motifs.

We further carried out scanning transmission electron microscopy (STEM) experiments to analyze the structure of the 2% Ni/ α -MoC catalyst in real space at the atomic scale. A nanoporous structure is clearly demonstrated by the large-scale Z-contrast STEM image (Figure 2a). The high-magnification high-angle annular dark-field (HAADF) image (Figure 2b) and the simultaneously acquired bright-field (BF) image (Figure 2c) show that the porous structure consists of aggregates of α -MoC particles with 5–10 nm size. To identify the spatial distribution of Ni species on the α -MoC, we performed Zcontrast STEM-HAADF imaging with simultaneous characteristic X-ray energy-dispersive spectroscopy (EDS) mapping. The elemental mapping results (Figure 2, parts e and f) indicate that Ni is homogeneously distributed on the surface of α -MoC without obvious aggregation. Similar homogeneous Ni distribution was also observed in the 0.5% Ni/ α -MoC sample as shown in Figure S4.

Since Ni has a lower atomic number than Mo, it is hard to unambiguously visualize Ni atoms on the α -MoC substrate in the Z-contrast HAADF images.²⁰ Instead, we performed aberration-corrected STEM imaging with simultaneous atomic-resolution electron energy-loss spectroscopy (EELS) mapping. As the L_{2.3} peaks of Ni do not overlap with the coreloss peaks of Mo and C in EELS,²⁵ it gives us the opportunity to "see" the light transition metal atoms on the heavy substrate and even analyze their electronic structure via EELS fine structures. As shown in Figure 2h, the majority of the Ni loading is atomically dispersed on the α -MoC substrate in the 2% Ni/ α -MoC sample, with some small subnanometer clusters observed very occasionally. Parts j and k of Figure 2 illustrate the atomic-scale EELS mapping results from one of the isolated Ni atoms. As shown by the extracted spectra in Figure 2k, Ni L signals are clearly observed at the central pixel (red), while the signal almost vanishes at the surrounding pixels 0.15 nm apart. This indicates that the Ni signal is highly localized within a single mapping pixel, as in the form of an atomically dispersed Ni atom (Figure S5). In order to analyze the valence state of these isolated Ni atoms, we turned to the fine structure of Ni L edge EELS. The L_3/L_2 ratio in EELS is a commonly used parameter to characterize the valence state of transition metals.²⁶ As shown in Figure 2l and Figure S6, the sum spectrum from 33 isolated Ni₁ atoms in 2% Ni/ α -MoC matches better to the reference spectrum of metallic Ni than NiO, indicating that the atomically dispersed Ni species are closer to the metallic state, consistent with the XAFS result. When the Ni loading is increased to 5% and 7%, in addition to the Ni single atoms, we start to observe aggregates of Ni clusters and the formation of Ni nanoparticles that are 2-5 nm in size (Figure S7).

We evaluated the catalytic performances of a few transition metal/ α -MoC catalysts in the aqueous-phase reforming of methanol (APRM) reaction for hydrogen production. Compared with the bare supports, only the introduction of nickel exhibited significant activity promotion among the tested 3d metals, with 1% Ni/ α -MoC showing a more than 5

pubs.acs.org/JACS



Figure 3. Catalytic performance and stability of Ni/ α -MoC catalysts. (a) Average catalytic activity of Ni/ α -MoC with different Ni loadings of 0%, 0.5% (0.33%), 1.0% (0.66%), 1.5% (1.3%), 2.0% (2.2%), 3.0% (3.1%), 5.0% (5.0%), and 7.0% (7.0%) at 240 °C with $n_{CH30H}/n_{H2O} = 1:1$ in 2 h; the exact loadings of Ni measured by ICP-AES are listed in the parentheses. (b) Approaching "real" APRM on 2% Ni/ α -MoC [$n(CH_3OH)/n(H_2O) = 1:1$]. TTN: total turnover number.



Figure 4. In situ XPS characterization of the 2% Ni/ α -MoC catalyst under methanol and water reaction condition. (a) The profiles of Ni 2p, C 1s, and Mo 3d were presented under different treatment conditions (activated catalyst and after the treatment of reaction atmosphere at 50, 150, and 240 °C, respectively. The incident X-ray photon energy is 1460 eV). (b) The Ni 2p XPS profiles of different 2% Ni/ α -MoC samples, which are passivated, activated, and under 240 °C reaction condition, respectively.

times higher hydrogen evolution rate than the corresponding supports (Table S4). Therefore, only the nickel-based catalysts were used for further performance optimization. The evaluation of the methanol-water ratio and reaction temperature both indicated that high methanol concentration and high temperature tend to facilitate hydrogen production over the Ni/ α -MoC catalyst (Figure S8, parts a and b). Under the optimal reaction condition (methanol-water molar ratio = 1, 240 °C), the average hydrogen production rate of 2% Ni/ α -MoC reached 171 μ mol/g/s (Table 1, entry 1) in a 2 h APRM reaction, which is about 6 times higher than that of the noble metal 2% Pt/Al₂O₃ catalyst¹³ (Table 1, entry 2) and more than 1 order of magnitude higher than conventional 2% Ni/TiO₂ (Table 1, entry 5), 2% Ni/SiO₂ (Table 1, entry 6), and other reported nickel-based catalysts²⁷ (Table 1, entries 8-10) under the same reaction condition. The activity of 2% Ni/ α -MoC is even higher than that of the best copper-based methanol steam reforming catalysts reported in literature (Table 1, entry 9).²⁸⁻³⁰ Additionally, the selectivity of 2% Ni/ α -MoC catalyst to the byproduct CO is 0.7%, which is only $\frac{1}{20}$ of the value of those conventional nickel oxide catalysts, although the selectivity of CH_4 is relatively high (~20%), as commonly seen in conventional Ni catalysts. In addition, the 2% Ni/ α -MoC catalyst shows high structural stability in the

aqueous phase. The XRD characterization proves that the catalyst maintains the face-centered cubic (fcc) α -MoC crystal structure after 240 °C reaction (Figure S8c).

The relationship between Ni loading and nickel-normalized activity (i.e., average turnover frequency, termed as ATOF), as well as the mass-specific activity of the Ni/ α -MoC catalysts, was studied (Figure 3a). At high Ni loading, e.g., 5% or higher, the ATOF is relatively low. For example, the ATOF for the 7% Ni/ α -MoC catalyst is 305 h⁻¹. The ATOF increases with the decrease of Ni loading, reaching 712 h⁻¹ for 5% Ni/ α -MoC and 1228 h^{-1} for 3% Ni/ α -MoC. From the STEM and EXAFS data, it is clear that the density of aggregated Ni species, i.e., clusters and small particles, increases at high Ni loading. This suggests that, while the atomically dispersed Ni species, clusters, and particles are all active for the APRM reaction, the atomically dispersed Ni species, i.e., Ni₁- C_x motif over α -MoC, is the most active site for this reaction. Indeed, when we further decreased the loading of Ni to 2 wt %, where the Ni-Ni coordination vanished and the almost full atomic dispersion of Ni was reached with highest surface coverage of Ni_1-C_r motif (Figure 1d), the ATOF reached a maximum of ~1700 h^{-1} , which is the highest for the reported non-noble-metal catalysts. Significantly, for catalysts with even lower Ni loading, a relatively constant ATOF with that of 2% Ni/ α -MoC is observed, strongly indicating that a full atomic dispersion is

Journal of the American Chemical Society

pubs.acs.org/JACS

Article



Figure 5. Structural models of Ni₁/ α -MoC(111) and the reaction path for hydrogen production from methanol and water. The top and side views for the six different models of Ni₁/ α -MoC(111), in which the subscripts of (a) C, (b) step-C, and (c) kink-C represent the Ni₁ atom being surrounded by the C atoms, but on top, step, and kink sites of α -MoC(111), respectively, and the subscripts of (d) Mo, (e) step, and (f) kink in these models represent the Ni₁ atom being adsorbed on the top, step, or kink sites of the α -MoC(111) surface. (g) Energy profiles for CH₃OH dissociation into CO and H atoms on α -MoC(111), Ni(111), and Ni_{kink}/ α -MoC(111) surfaces. (h) The energy profiles for water dissociation over α -MoC(111) and Ni(111) surfaces. (i) The most favorable energy profiles for the WGS path over Ni(111) and Ni_{kink}/ α -MoC(111) surfaces. The Mo, Ni, C, O, and H atoms are shown in cyan, light purple, gray, red, and white, respectively. In order to make a distinction, the Mo, Ni, and C atoms in the step and kink layers are in blue, dark purple, and orange, respectively, while the C atoms from CH₃OH are in black.

reached when the loading of Ni is lower than 2%, in good agreement with the EXAFS and STEM observations. These catalytic data also suggest that the chemical environment of the supported Ni species is almost identical on α -MoC at this low Ni loading region (0.5–2%).

Interestingly, the mass-specific activity starts at a very low value (26 μ mol/g/s) at low Ni loading (0.5%) and increases sharply with the increase of Ni loading (105 μ mol/g/s for 1.5% Ni/ α -MoC), reaching a maximum of around 180 μ mol/g/s at 2–3% Ni loading. The linear relationship of the H₂ production rate and the varied Ni loadings from 0% to 2% suggests that the active sites of methanol reforming over these catalysts are almost identical and uniformly dispersed on the support, which serves as another solid evidence that the Ni species are atomically dispersed over α -MoC below 2 wt %. Furthermore, the hydrogen production rate gradually decreases with further increase of the Ni loading (100 μ mol/g/s over the 7% Ni/ α -MoC catalyst). Clearly, the 2% Ni/ α -MoC catalyst, which has the highest density of atomically dispersed Ni₁–C_x motifs and

almost no Ni clusters, is the optimal catalyst for APRM that ensures both a high ATOF and mass-specific activity. Further increasing the Ni loading cannot compensate for the drastic activity drop at each Ni site when Ni clusters or particles are formed, causing the loss of the mass-specific activity. In a 10cycle long-term stability test, the 2% Ni/ α -MoC achieved a total turnover number of ~10 000, i.e., each Ni site converts ~10 000 H₂ molecules, demonstrating the excellent stability of the 2% Ni/ α -MoC under the optimized reaction condition (Figure 3b, Figure S9).

In situ XPS was applied to reveal the evolution of the surface structure of the 2% Ni/ α -MoC catalyst under the reaction atmosphere at elevated temperatures. As shown in Figure 4a, the Mo $3d_{5/2}$ and C 1s edges are located at 228.3 and 283.8 eV, respectively, after activation,^{10,31} which can be assigned to the binding energy (BE) of molybdenum carbide. These two edges kept relatively unchanged under *in situ* reaction at various temperatures, suggesting that most of the Mo species remained intact under reaction conditions. Only a slight amount of high-

adsorption/transformation of the reactants and reaction intermediates. As the Ni species are dominated by the Ni_1-C_r motif, a slight change in the chemical environment at the Ni_1-C_x sites or the Ni₁/ α -MoC interface may impose a substantial impact on the electronic structure and the binding energy. At a reaction temperature of 50 °C, where the reaction is hardly ignited, the Ni 2p XPS spectrum is almost identical to that of the native 2% Ni/ α -MoC catalyst. With the increase of reaction temperature to 150 °C, besides the emergence of a small amount of high valence state Mo species, we notice that the Ni 2p peak moved marginally to higher binding energy, in reference to the native catalyst. This trend became more obvious at 240 °C, and a positive shift of the Ni 2p XPS peaks by 0.9 eV (from 853.2 to 854.1 eV) was observed (Figure 4b), which, however, is still far from being oxidized into the Ni²⁺ state. During the APRM reaction, both the α -MoC and Ni₁- C_x motif may well participate in the adsorption and activation of oxygenated reactants. Indeed, from the in situ XPS results we can clearly see the charge transfer and interaction of the

reactants/intermediates with the reactive sites during the

reforming reaction of methanol and water, which is in good agreement with simulation results (see Figures S10 and S11). DFT calculations were performed to further understand the reactivity of the Ni/ α -MoC catalysts. We optimized six different adhesion sites of Ni₁ species on α -MoC(111) (Figure 5a-f; the detail information of the six models is listed in Table S5) to simulate the Ni₁ $-C_x$ motif, and the adsorption energies of the atomic Ni are listed in the corresponding parentheses, which can estimate the relative stability. On the basis of the experimental results (Table S2, EXAFS fitting results) and the stability consideration of the six Ni/ α -MoC models, we chose the Ni_{kink-C}/ α -MoC(111) (model 5c, Ni bonded with three C atoms) as one of the possible models to represent the Ni/ α -MoC catalyst for APRM. Further calculations show that the boundary C atom adjacent to the Ni1 is apt to be removed by hydrogen produced in the reaction (Figure S12), and the structure transforms into the Ni_{kink}/ α -MoC(111) configuration (model 5f, still Ni_1-C_r configuration; see also Figure S13), which was therefore used in the electronic property analysis of the catalyst (see Figure S14) and mechanism calculations of the APRM reaction.

For comparison, α -MoC(111) and Ni(111) surfaces were used as reference catalysts for the APRM reaction, representing pure α -MoC and conventional Ni/SiO₂ catalysts (Figure 5). For methanol decomposition, the detailed calculations show that the rate-determining step on the models is the second step, $CH_3O \rightarrow CH_2O + H$ (Figure 5g). Interestingly, the energy barrier on Ni_{kink}/ α -MoC(111) is much lower than those of α -MoC(111) and Ni(111) (0.73 vs 1.30 and 1.42 eV), indicating that the pure α -MoC and Ni catalysts are not favorable for methanol activation, while the Ni/ α -MoC with Ni_1-C_x motif is efficient in this step. We then investigated the important successive steps of water dissociation (Figure 5h) over α -MoC(111) and Ni(111), as well as the CO reforming (Figure S15 and Figure 5i) with hydroxyls or oxygen atom formed from water dissociation. The results show that the product from methanol decomposition, CO, first should migrate on the top Ni site (Figure S16), and the path of CO + 2OH \rightarrow CO₂ + H₂O will occur favorably on the boundary of the Ni site in Ni_{kink}/ α -MoC(111), while the preferable reaction path on Ni(111) is CO + O \rightarrow CO₂. Significantly, the reforming barrier on the Ni_{kink}/ α -MoC(111) is 1.13 eV, as compared to 1.60 eV on the Ni(111) surface. When all these results are combined, it can be found that, although the pure α -MoC(111) can reform water into OH with a very low barrier of 0.56 eV, the methanol activation step is extremely difficult with a high barrier (1.30 eV), and thus, the rate constant ratio of water and methanol decomposing $(k_{\rm H2O}/k_{\rm CH3OH})$ is very high (6.56×10^8) ,¹² i.e., the α -MoC surface will be almost fully covered with OH, leading to the low activity for the whole reaction. Only the Ni_{kink}/ α -MoC(111) model with the maximized Ni1 and MoC interface has the optimal reactivity both for methanol activation and the subsequent reforming reaction, and this accounts for the exceptional reactivity in hydrogen production from the methanol reaction with water.

CONCLUSIONS

In summary, a new Ni/ α -MoC catalyst with a high density of isolated Ni atoms stabilized by the carbon bridges over the α -MoC host (Ni₁-C_x motif) has been synthesized and used for efficient hydrogen production from aqueous-phase reforming of methanol. Under the optimal condition, the ATOF of the catalyst reached 1800/h at 240 °C, which is almost 6 times higher than that of the Pt/Al₂O₃ catalyst. Our catalyst showed low selectivity toward the undesired CO byproduct and excellent stability in the aqueous phase. The excellent synergy of the efficient C–H bond dissociation and CO reforming over the atomically dispersed Ni, as well as the highly efficient O–H activation over molybdenum-terminated α -MoC, is the key for the extraordinary catalytic performance in this reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c10776.

Supplementary methods, discussions, additional figures and tables including properties of Ni/ α -MoC catalysts, structural characterization, models, performance evaluation, DFT calculations, additional experimental data, and references (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Ding Ma Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering and College of Engineering, and BIC-ESAT, Peking University, Beijing 100871, China; orcid.org/0000-0002-3341-2998; Email: dma@pku.edu.cn
- Wu Zhou School of Physical Sciences and CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences, Beijing 100049, China; CAS Center for Excellence in Topological Quantum Computation, University of Chinese Academy of Sciences, Beijing 100049, China; Email: wuzhou@ucas.ac.cn
- Rui Gao State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China; National Energy Center for Coal to Liquids, Synfuels China Company Limited, Beijing 101400, China; School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China; Email: gaorui@imu.edu.cn

Journal of the American Chemical Society

pubs.acs.org/JACS

Authors

- Lili Lin Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering and College of Engineering, and BIC-ESAT, Peking University, Beijing 100871, China; College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China
- **Qiaolin Yu** Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering and College of Engineering, and BIC-ESAT, Peking University, Beijing 100871, China
- Mi Peng Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering and College of Engineering, and BIC-ESAT, Peking University, Beijing 100871, China
- Aowen Li School of Physical Sciences and CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences, Beijing 100049, China
- Siyu Yao Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering and College of Engineering, and BIC-ESAT, Peking University, Beijing 100871, China
- Shuheng Tian Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering and College of Engineering, and BIC-ESAT, Peking University, Beijing 100871, China
- Xi Liu School of Chemistry and Chemical, In-situ Center for Physical Science, Shanghai Jiao Tong University, Shanghai 200240, China
- Ang Li Beijing Key Laboratory of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100024, China; ⊙ orcid.org/0000-0002-9802-9359
- Zheng Jiang Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China; Ocid.org/ 0000-0002-0132-0319
- Xiaodong Han Beijing Key Laboratory of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100024, China; orcid.org/0000-0002-0193-1291
- Yong-wang Li State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China; National Energy Center for Coal to Liquids, Synfuels China Company Limited, Beijing 101400, China
- Xiao-dong Wen State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China; National Energy Center for Coal to Liquids, Synfuels China Company Limited, Beijing 101400, China

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c10776

Author Contributions

•Lili Lin, Qiaolin Yu, Mi Peng, and Aowen Li contributed equally to this work.

Notes

The authors declare no competing financial interest.

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGMENTS

This work received financial support from the Natural Science Foundation of China (21725301, 21932002, 21821004, 21673273, 21872163, 22072090, 21802076, 22002140), the National Key R&D Program of China (2017YFB0602200, 2018YFA0305800), and the Beijing National Laboratory for Molecular Science (BNLM202011). The X-ray absorption spectroscopy experiments were conducted at the Shanghai Synchrotron Radiation Facility. The XPS measurements were conducted at the National Synchrotron Radiation Facility (Hefei). Ding Ma acknowledges the support from the Tencent Foundation through the XPLORER PRIZE. Wu Zhou acknowledges the support from Key Research Program of Frontier Sciences, Chinese Academy of Sciences, and the Beijing Outstanding Young Scientist Program (BJJWZYJH01201914430039). The Young Elite Scientist Sponsorship Program by CAST, no. 2019QNRC001, is also acknowledged. We thank Mr. Meng Gao of UCAS for assistance on developing the script for EELS data analysis and Professor Zhi Liu (SHST) for helpful discussion.

REFERENCES

(1) Cohen, R. L.; Wernick, J. Hydrogen storage materials: properties and possibilities. *Science* **1981**, *214* (4525), 1081–1087.

(2) Seayad, A. M.; Antonelli, D. M. Recent advances in hydrogen storage in metal-containing inorganic nanostructures and related materials. *Adv. Mater.* **2004**, *16* (9-10), 765–777.

(3) Deng, Z. Y.; Ferreira, J. M.; Sakka, Y. Hydrogen-Generation Materials for Portable Applications. *J. Am. Ceram. Soc.* **2008**, *91* (12), 3825–3834.

(4) Jacobson, M.; Colella, W.; Golden, D. Cleaning the air and improving health with hydrogen fuel-cell vehicles. *Science* **2005**, *308* (5730), 1901–1905.

(5) Sharaf, O. Z.; Orhan, M. F. An overview of fuel cell technology: Fundamentals and applications. *Renewable Sustainable Energy Rev.* **2014**, *32*, 810–853.

(6) Christensen, C. H.; Johannessen, T.; Sørensen, R. Z.; Nørskov, J. K. Towards an ammonia-mediated hydrogen economy? *Catal. Today* **2006**, *111* (1), 140–144.

(7) Palo, D. R.; Dagle, R. A.; Holladay, J. D. Methanol steam reforming for hydrogen production. *Chem. Rev.* 2007, 107 (10), 3992–4021.

(8) Yadav, M.; Xu, Q. Liquid-phase chemical hydrogen storage materials. *Energy Environ. Sci.* **2012**, *5* (12), 9698–9725.

(9) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.-J.; Junge, H.; Gladiali, S.; Beller, M. Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide. *Nature* **2013**, 495 (7439), 85.

(10) Lin, L.; Zhou, W.; Gao, R.; Yao, S.; Zhang, X.; Xu, W.; Zheng, S.; Jiang, Z.; Yu, Q.; Li, Y.-W.; Shi, C.; Wen, X.-D.; Ma, D. Low-temperature hydrogen production from water and methanol using Pt/ α -MoC catalysts. *Nature* **2017**, *544* (7648), 80.

(11) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. Raney Ni-Sn catalyst for H2 production from biomass-derived hydrocarbons. *Science* **2003**, *300* (5628), 2075–7.

(12) Davda, R. R.; Dumesic, J. A. Catalytic reforming of oxygenated hydrocarbons for hydrogen with low levels of carbon monoxide. *Angew. Chem.* **2003**, *115* (34), 4202–4205.

(13) Cortright, R. D.; Davda, R. R.; Dumesic, J. A. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* **2002**, *418* (6901), 964–7.

(14) Shabaker, J.; Davda, R.; Huber, G.; Cortright, R.; Dumesic, J. Aqueous-phase reforming of methanol and ethylene glycol over alumina-supported platinum catalysts. *J. Catal.* **2003**, *215* (2), 344–352.

Journal of the American Chemical Society

Article

(15) Deng, Y.; Gao, R.; Lin, L.; Liu, T.; Wen, X. D.; Wang, S.; Ma, D. Solvent Tunes the Selectivity of Hydrogenation Reaction over alpha-MoC Catalyst. *J. Am. Chem. Soc.* **2018**, *140* (43), 14481–14489.

(16) Clausen, B. S.; Topsøe, H.; Frahm, R. Application of Combined X-Ray Diffraction and Absorption Techniques for in Situ Catalyst Characterization. *Adv. Catal.* **1998**, *42*, 315.

(17) Schweitzer, N. M.; Schaidle, J. A.; Ezekoye, O. K.; Pan, X.; Linic, S.; Thompson, L. T. High activity carbide supported catalysts for water gas shift. *J. Am. Chem. Soc.* **2011**, *133* (8), 2378–81.

(18) Chastain, J.; King, R. C.; Moulder, J. Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data; Physical Electronics Division, Perkin-Elmer Corporation: Eden Prairie, MN, 1992.

(19) Lin, L.; Yao, S.; Gao, R.; Liang, X.; Yu, Q.; Deng, Y.; Liu, J.; Peng, M.; Jiang, Z.; Li, S.; et al. A highly CO-tolerant atomically dispersed Pt catalyst for chemoselective hydrogenation. *Nat. Nanotechnol.* **2019**, *14* (4), 354.

(20) Yao, S.; Lin, L.; Liao, W.; Rui, N.; Li, N.; Liu, Z.; Cen, J.; Zhang, F.; Li, X.; Song, L.; et al. Exploring Metal–Support Interactions To Immobilize Subnanometer Co Clusters on γ – Mo2N: A Highly Selective and Stable Catalyst for CO2 Activation. ACS Catal. 2019, 9 (10), 9087–9097.

(21) Wei, H.; Liu, X.; Wang, A.; Zhang, L.; Qiao, B.; Yang, X.; Huang, Y.; Miao, S.; Liu, J.; Zhang, T. FeO x-supported platinum single-atom and pseudo-single-atom catalysts for chemoselective hydrogenation of functionalized nitroarenes. *Nat. Commun.* **2014**, *5*, 5634.

(22) Yang, S.; Kim, J.; Tak, Y. J.; Soon, A.; Lee, H. Single-atom catalyst of platinum supported on titanium nitride for selective electrochemical reactions. *Angew. Chem., Int. Ed.* **2016**, 55 (6), 2058–2062.

(23) Yang, W.; Rehman, S.; Chu, X.; Hou, Y.; Gao, S. Transition metal (Fe, Co and Ni) carbide and nitride nanomaterials: structure, chemical synthesis and applications. *ChemNanoMat* **2015**, *1* (6), 376–398.

(24) Schaefer, Z. L.; Weeber, K. M.; Misra, R.; Schiffer, P.; Schaak, R. E. Bridging hcp-Ni and Ni3C via a Ni3C1-x Solid Solution: Tunable Composition and Magnetism in Colloidal Nickel Carbide Nanoparticles. *Chem. Mater.* **2011**, *23* (9), 2475–2480.

(25) Egerton, R. F. Electron energy-loss spectroscopy in the TEM. Rep. Prog. Phys. 2009, 72 (1), 016502.

(26) Leapman, R. D.; Grunes, L. A.; Fejes, P. L. Study of theL23edges in the3dtransition metals and their oxides by electronenergy-loss spectroscopy with comparisons to theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1982**, 26 (2), 614–635.

(27) Qi, C.; Amphlett, J. C.; Peppley, B. A. Methanol steam reforming over NiAl and Ni (M) Al layered double hydroxides (M= Au, Rh, Ir) derived catalysts. *Catal. Lett.* **2005**, *104* (1–2), 57–62.

(28) Sá, S.; Silva, H.; Brandão, L.; Sousa, J. M.; Mendes, A. Catalysts for methanol steam reforming—A review. *Appl. Catal., B* **2010**, 99 (1–2), 43–57.

(29) Agrell, J.; Birgersson, H.; Boutonnet, M. Steam reforming of methanol over a Cu/ZnO/Al2O3 catalyst: a kinetic analysis and strategies for suppression of CO formation. *J. Power Sources* **2002**, *106* (1-2), 249–257.

(30) Shishido, T.; Yamamoto, Y.; Morioka, H.; Takaki, K.; Takehira, K. Active Cu/ZnO and Cu/ZnO/Al2O3 catalysts prepared by homogeneous precipitation method in steam reforming of methanol. *Appl. Catal., A* **2004**, *263* (2), 249–253.

(31) Yao, S.; Zhang, X.; Zhou, W.; Gao, R.; Xu, W.; Ye, Y.; Lin, L.; Wen, X.; Liu, P.; Chen, B.; et al. Atomic-layered Au clusters on α -MoC as catalysts for the low-temperature water-gas shift reaction. *Science* **2017**, 357 (6349), 389–393.